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THE ELECTRONIC SPECTRA OF SOME TRISUBSTITUTED BENZENES IN DIFFERENT STATES-I*

T. N. MISRA

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32

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ABSTRACT. The near ultraviolet absorption spectra of 1, 2, 3-trichloro- and 1, 2, 3-trihydroxybenzene have been studied in the liquid state, solid state at room temperature and at −180°C and also in rigid glass media in alcohol at the same temperature. In the liquid state and in the solid state at room temperature both the substances yield weak, broad, diffuse bands showing the characteristics of forbidden transition as in free molecules due to cancellation of three migration moment vectors. At −180°C, the transition becomes allowed and the band systems consists of sharp bands with the 0, 0 band at 35347 cm^{-1} for 1, 2, 3-trichlorobenzene and at 36109 cm^{-1} for 1, 2, 3-trihydroxybenzene. The other bands are satisfactorily assigned to excited state vibrational frequencies. The structure of the bands in the rigid glass at −180°C is similar to that of pure crystals at same temperature except that it is at higher energy region and in 1, 2, 3-trihydroxybenzene the bands are sharper.

These results indicate that a perturbation on the energy states of these molecules occur at −180°C. It has been pointed out that the interaction of permanent dipoles of the neighbouring molecules on the transition moment of the molecules in the lattice might play a dominant role in determining the energy states of molecular crystals.

INTRODUCTION

The intensity of absorption and structure of bands in the electronic spectra of trisubstituted benzenes are known to depend on the symmetry of the molecules. In symmetrical trisubstituted benzenes the 0,0 band in the near ultraviolet absorption spectra is forbidden in the vapour state as in benzene, whereas in the spectra of 1, 2, 4-trisubstituted benzenes the 0,0 band is allowed (Sponer, 1947). Sklar (1942) calculated the contributions from the substituents to the migrational transition moment and found that they annul one another in the first order in 1, 2, 3-trisubstituted benzenes, when the substituents at the positions are the same. Thus theoretically, the spectra should appear in these cases only through vibrational moments i.e. by distorting the symmetry of the molecule through excitation of vibrations. In 1, 2, 4-trisubstituted benzene, however, the three migration moment vectors are added up to give a large resultant migration moment and the spectra are expected to be allowed with a strong 0,0 band. The influence of intermolecular field on the electronic spectra of a few trisubstituted benzene has recently been studied by a number of workers. It has been observed

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that the symmetrically forbidden transitions in 1,3,5-trichlorobenzene (Banerjee, 1957) and 1,3,5-trimethylbenzene (Sen, 1959) become allowed in pure crystals when cooled to-180°C. Schnepp (1959) studied the polarised electronic spectra of orientated single crystal of 1,3,5-trichlorobenzene at -180°C and concluded that the appearence of the 0,0 band was due to change in symmetry of the molecule. Roy (1958) observed that in the spectrum of the substance dispersed in rigid glass media at -180°C also, the 0,0 band was present. In the present work, investigations on the electronic spectra of trisubstituted benzenes in different states have been extended to the molecules of 1,2,3-trichlorobenzene and 1,2,3-trihydroxybenzene.

EXPERIMENTAL

The experimental set up was the same as described in an earlier paper (Misra, 1960). Chemically pure 1,2,3-trichloro-and trihydroxybenzene supplied by Dr. Theodor Schuchardt of Munich and E. Merck & Co respectively were repeatedly crystallised from solutions in alcohol and the crystals were further purified by vacuum sublimation before use.

Thin films of the substances of thicknesses of the order of a few microns were required to produce bands in the solid state. To study the absorption spectra in the liquid state, the thin film of substances enclosed between two quartz plates was placed in a heating chamber which was kept at temperatures about 5°C above the respective melting points of the substances.

The solvent used to study the absorption spectra of the substances in solution and in rigid glass media at -180°C was ethyl alcohol. The solvent was found to produce no absorption band in the region under consideration. A brass cell of thickness 1 cm provided with quartz windows was used to study the absorption spectra of the substance in solution and in rigid glass and the strength of the solution was .01% by weight in each case.

Spectrograms were taken on Agfa Isopan films backed by a metal sheet with a Hilger E 1 spectrograph giving a dispersion of the order of 3 A per mm. in the region of 2600 A. Iron arc spectrum was photographed on each spectrogram as a comparison. Microphotometric records were taken with a Kipp and Zonen self-recording microphotometer. The absorption spectra were calibrated with the help of microphotometric records of iron arc lines using the method described in an earlier paper (Sirkar and Misra, 1959).

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra of the 1,2,3, -trichlorobenzene and 1,2,3-trihydroxybenzene are given in Figs. 1—4 and the positions of the bands in wave numbers, their visual strengths of absorption and probable assignments are given in Tables 1-111.

The results have been discussed in the following sections.

1,2,3-*Trichlorobenzene*

The near ultraviolet absorption spectra of 1,2,3-trichlorobenzene along with those for 1,3,5- and 1,2,4-trichlorobenzene were studied by Conrad-Billroth (1932) in hexane solution and several distinct maxima were observed. Though the absorption is strong in the case of 1, 2, 4-trichlorobenzene, the other two compounds exhibit very feeble absorption. This shows the characteristics of forbidden transition. The absorption spectrum of 1, 2, 3-trichlorobenzene in the vapour phase was studied by Sponer (1947) who observed that the structure of the spectrum was different from that of the other two isomers. It consists of three broad, diffuse and weak bands which are separated from each other by about 995 cm^{-1}. No band due to $1\rightarrow0$ transition in the vapour phase was observed and therefore it was suggested that the 0,0 band might be present in the first weak group. The centre of the first group is at about 35910 cm^{-1}, but as the transition is ordinarily forbidden, the 0,0 band cannot be strong and therefore it cannot be at the centre of the first band. It has been observed in the present investigation that in the liquid state at 70°C also 1, 2, 3-trichlorobenzene shows three broad bands (Fig. 1, Table 1), the centre of the bands being at 35535 cm^{-1}, 36607 cm^{-1} and 37681 cm^{-1}, respectively the difference between successive bands

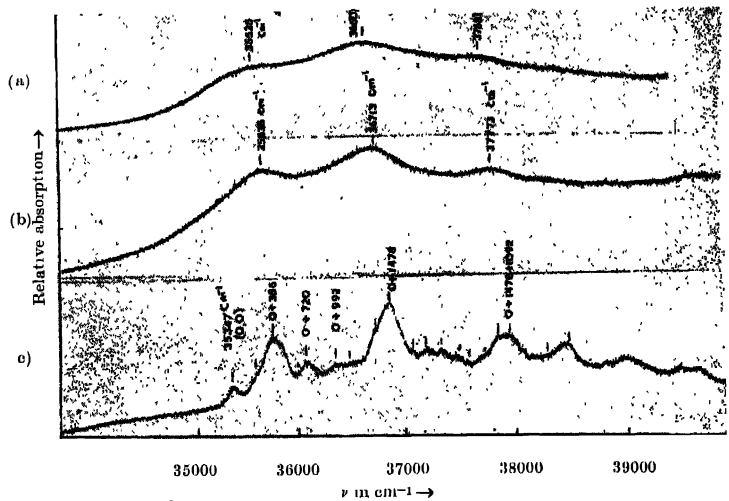

Fig. 1. Microphotometric records of the ultraviolet absorption spectra of 1,2,3-trichloro benzene in different states.
(a) liquid state at 70°C. (b) solid state at 32°C. (c) solid state at −180°C.

TABLE] I

Ultraviolet absorption bands of 1, 2, 3-trichlorobenzene in different states

Liquid at 70°C		Solid at 32°C		Crystal at −180°C	
Wave No. in cm^{-1}	Difference	Wave No. in cm^{-1}	Difference	Wave No. in cm^{-1}	Assignment
35535 (vs)		35638 (s)		35347 (ms)	0,0
	1072		1075		
				35616 (w)	0+269
36607 (s)		36713 (s)			
	1072		1075	35733 (vs)	0+386
37681 (s)		37773 (s)		35837 (w	0+490
				36002 (vw)	0+269 +386
				36067 (ms)	0+269 +490
					0+720
				36223 (w)	0 + 386+ 490
				36339 (m)	0 + 992
				36439 (m)	0 + 1092
				36557 (vw)	0+1210
				36725 (mw)	0 +992 + 386
					0+1092+269
				36825 (vs)	0+1478
					0 +1092 +386
				36929 (w)	0+1092+490
				37059 (mw)	0+720+992
				37159 (m)	0+720+1092
				37316 (m)	0 + 1092+490+386
					0+1478+490
					0 +2×992
				37431 (m)	0 + 992+1092
				37531 (mw)	0 + 2×1092
				37649 (w)	0 +1092+1210
				37717 (w)	0 + 2×992 + 386
				37817 (m)	0 + 2×1092+269
					0+1092+992+386
				38033 (w)	0+2×1092+490
					0+1478+1210
				38151 (w)	0 +1092+992+720
				38251 (vw)	0 + 2×1092 +720
				38413(s)	0+2×1092 +386
					+490
					0+1478+1092+490
				38523 (w)	0+2×1092+992
				38800 (m)	0+2×992+1478
					0+2×992+1092+
					386
				39009 (ms)	0+2×1092+1478
				39499 (m)	0+2×992+2+1092

being about 1072 cm^{-1}. Thus it appears that on liquefaction of the vapour, the band system is shifted by about 375 cm^{-1} towards red.

When the liquid is solidified at the room temperature the bands become a little sharper but no further resolution of the structure of the bands takes place and the spectrum consists of three broad bands as in the liquid state, the centres of the bands being now at 35638 cm^{-1}, 36713 cm^{-1} and 37773 cm^{-1} respectively. Thus the band system is shifted by about 272 cm^{-1} towards red from its position in the vapour phase.

When the temperature of the crystals is lowered to −180°C each of the three bands is split up into a number of bands and the spectrum consists of strong sharp bands as in the case of allowed transition. The very strong band at 35733 cm^{-1} was approximately at the centre of a number of bands. The first band on the long wavelength side at 35347 cm^{-1} was taken as the 0, 0 band of the system. All the other bands in the spectrum could then be explained satisfactorily in terms of excited state frequencies 269, 386, 490, 992, 1092, 1210 and 1478 cm^{-1} and their combinations. These frequencies correspond respectively to the ground state Raman frequencies 333, 486, 505, 1076, 1151, 1248 and 1554 cm^{-1} as given in Landolt-Bornstein's Tables (1951). No Raman-shift of 720 cm^{-1} was given

TABLE II

Ultraviolet absorption bands of 1, 2, 3-trichlorobenzene in alcohol

In solution at 32°C		In rigid glass media at −180°C	
Wave No. in cm^{-1}	Difference	Wave No. in cm^{-1}	Assignment
		35463 (s)	0, 0
		35719 (w)	0+256
35652 (s)			
	1050	35844 (vs)	0+381
36702 (vs)		35947 (w)	0+484
	1050		
		36197 (ms)	0+256+484
37753 (s)			0+734
		36538 (ms)	0+1075
		36903 (vs)	0+1440
		37177 (m)	0+256+381+1075
		37281 (m)	0+734+1075
		37386 (m)	0+484+1440
		37870 (m)	0+2×1075+256
		37997 (ms)	0+2×1075+381
			0+1440+1075
		38479 (ms)	0+2×1075+381+484
			0+1440+1075+484
		39043 (ms)	0+2+1075+1440

in Landolt-Bornstein's Tables but such a frequency is usually observed in other 1, 2, 3-trisubstituted benzenes such as trimethylbenzene, trihydroxybenzene (Landolt-Bornstein's Table, 1951). Thus the very strong band at 35733 cm^{-1} which is at a distance of 386 cm^{-1} from the 0,0 band represents the centre of the broad band observed in the spectrum due to the crystal at room temperature. Hence the 0, 0 band is on the long wavelength side of the centre of the first broad band observed in the case of the liquid and it has been concluded that the 0, 0 band appears only when the crystals are cooled to —180°C.

When the substance is dissolved in alcohol, three broad bands, as those due to the liquid state and solid state at 32°C, are observed, the centres of the bands being at 35652 cm^{-1}, 36702 cm^{-1} and 37753 cm^{-1} respectively (Fig. 2 Table II). In hexane solution (Conrad-Billroth, 1932) the first broad band was approximately at 35700 cm^{-1}. Thus in alcohol solution at room temperature, the band system is shifted towards red from its position in hexane solution and it is approximately in the same position as in pure the spectum of crystals at the room temperature.

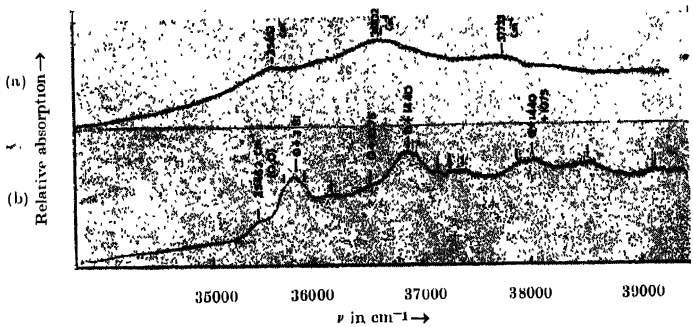

Fig. 2. Microphotometric records of the ultraviolet absorption spectra of 1,2,3-trichlorobenzene.
(a) alcohol solution at 32°C. (b) Rigid Glass Medium at —180°C.

The assignments of the bands due to crystals at —180°C are supported by the spectra of the substance dispersed in rigid glass medium in alcohol at —180°C. The structure of the bands in rigid glass is similar to that due to pure crystals at —180°C. The first band of medium strength is now at 35463 cm^{-1} and taking this as the 0, 0 band, the other bands can be assigned to upper state fundamentals 256, 381, 484, 734, 1075 and 1440 cm^{-1} and their combinations. Thus the 0, 0 band of 1, 2, 3-trichlorobenzene in frozen alcohol at —180°C is at a distance of 116 cm^{-1} on the high energy side of the 0, 0 band due to the pure crystals at —180°C and the upper state fundamentals in the two cases agree fairly well with each other.

Thus it is seen that in the spectra of the substance in rigid glass media at —180°C and also of the pure crystals at —180°C the strength of absorption is much larger than that in free molecules and the broad bands of crystals at room temperature are resolved into a number of sharp bands in the former case. In rigid glass, the bands are less sharp than in pure crystals at —180°C but the structure of the spectrum is the same in both the cases. These results indicate that transition which is forbidden in free molecules due to cancellation of three migrational moment vectors, becomes allowed probably due to some distortion in the symmetry of the molecules at —180°C. The weak 0, 0 band in the spectrum due to the crystals at —180°C indicate that though the transition is allowed at this temperature, the magnitude of the transition moment is very small and its interaction with the permanent dipole of the neighbouring molecule is expected to be very weak. It has been proposed by Sirkar (1962, 1963) that such interaction might be partly responsible for producing large splitting of electronic bands in crystals of polar molecules. In the present case, the interaction may be too weak to produce any detectable splitting of the bands and actually no splitting has been observed.

1,2,3-*Trihydroxybenzene*

Little work has been done on the electronic spectra of pyrogallol in the near ultraviolet region. Leonard Jurd (1957) observed the absorption maximum of the substance at 2670 A in solution in alcohol at room temperature. Shergina *et. al.* (1959)al so reported similar observations. In the present investigation, the ultraviolet absorption spectra of the substance were investigated in the liquid and solid states at room temperature and also at —180°C. The spectrum of the subatance in solution in alcohal at —180°C was also photographed in order to verify the assignments of the bands due to the polycrystalline mass at —180°C.

In the liquid state, a broad region of absorption extending from 35627 cm^{-1} to 38156 cm^{-1} was observed without any discrete structure. When the liquid was solidified at the room temperature, three broad bands were observed, the centres of the bands being at 35999 cm^{-1}, 36678 cm^{-1} and 37246 cm^{-1} respectively.

When the solid is cooled down to —180°C, the spectrum consists of strong but broad bands and eight strong bands are clearly resolved. No other bands were observed on the long wavelength side of the strong band at 36109 cm^{-1} and this was taken as the 0, 0 band of the system then the other bands represented and this was taken as the 0, 0 band of the system then the other bands represented excited state frequencies 429, 537, 675, 972, 1237 and 1463 cm^{-1} which correspond to the Raman frequencies 466, 573, 767, 1015, 1237 and 1473 cm^{-1} (Landolt-Bornstein's Tables 1951). A strong Raman line 1386 cm^{-1} has been reported in these Tables and the band due to the corresponding upper state frequency is

probably not resolved from the two bands representing the frequencies 1237 and 1463 cm^{-1}.

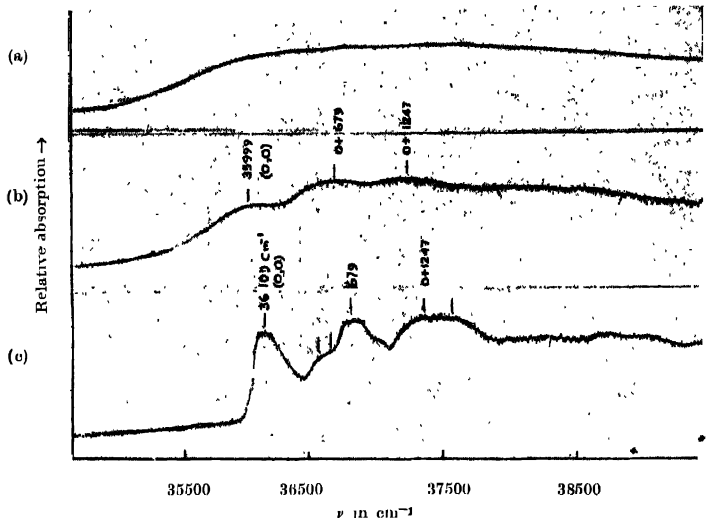

Fig. 3. Microphotometric records of the ultraviolet absorption spectra of 1,2,3-trihydroxybenzene in different states.
(a) liquid at 140°C (b) Solid at 32°C (c) solid at −180°C.

TABLE III

Ultraviolet absorption bands of pyrogallol

Liquid at 140°C	Solid at room temperature		Solid at − 180°C		Rigid glass at −180°C in alcohol	
	Wave No. in cm^{-1}	Assignment	Wave No. in cm^{-1}	Assignment	Wave No. in cm^{-1}	Assignment
	35999 (m)	0,0	36109 (vs)	0,0	35857 (s)	0,0
Broad absorption			36538 (m)	0 + 429	36273 (ms)	0+416
region	36678 (s)	0+679				
			36646 (m)	0+537	36392 (m)	0+535
extending from	37246 (s)	0+1247				
			36784 (vs)	0+675	36526 (ms)	0+669
35627 cm^{-1}			37081 (w)	0+972	37081 (s)	0+1224
to 38156 cm^{-1}			37346 (s)	0+1237	37274 (s)	0+1427
			37572 (s)	0+1463		

In the case of the solution in alcohol at —180°C, the structure of the spectrum resembles that due to pure crystals at —180°C except that in the latter case the bands are strong but quite broad while in the former case the bands are sharp. The first band on the long wavelength side assigned as the 0, 0 band in pure crystals of 1, 2, 3-trihydroxybenzene at —180°C is quite strong compared to that in 1, 2, 3-trichlorobenzene and the transition moment has a larger value in the former than in the latter molecule. The broadness of the bands probably indicates that the bands are split up in the spectrum due to pure crystals at —180°C and the split components are not resolved. The 0, 0 band in this case is at 35857 cm^{-1} and the other bands represent upper state fundamentals

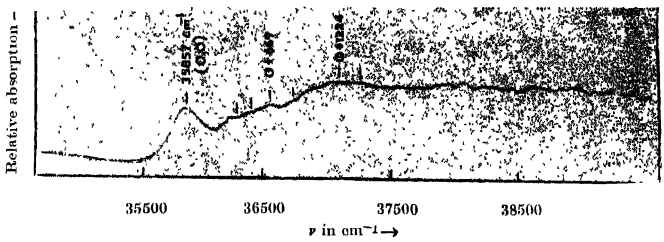

Fig. 4. Microphotometric records of ultraviolet absorption spectrum of 1,2,3-trihydroxy benzene in rigid glass medium at —180°C.

416, 535, 669, 1224 and 1427 cm^{-1} which agree fairly well with the values in the case of the pure crystals at —180°C. Thus the 0, 0 band in pure crystals at —180°C is shifted towards the higher energy region by about 252 cm^{-1} with respect to that due to rigid glass medium at the same temperature.

These results indicate that the symmetry of the molecule is distrubed at low temperature and the transition which is forbidden in the free molecule is made allowed as in the case of 1, 2, 3-trichlorobenzene. Further interaction of permanent dipoles of the neighbouring molecules on the transition moment of the molecules in the lattice plays a dominant role in determining the energy states of molecular crystals.

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